MODELLING THE ROLE OF ACIDIC SPECIES ON CO_2 CORROSION PREDICTION

MOHAMAD AZWAN BIN MOHD GHAZALI

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Faculty of Mechanical Engineering
UNIVERSITI MALAYSIA PAHANG

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ABSTRACT

The presence of acetic acid (HAc) in formation water of oil and gas reservoirs has long been suspected to contribute to the CO_2 corrosion rate. The prediction model has been developed based on mechanistic theories which is involved the fundamental of electrochemical reaction for partial cathodic and anodic process on the metal surface. By using this prediction model, the corrosion behaviour of carbon steel in the presence of HAc in combination with pH and temperature at simultaneously has been investigated. The corrosion prediction model was verified by comparing calculated corrosion rates with the corrosion data obtained from various literature sources and corrosion prediction software's and it's showed a good relationship in correlation and regression relationship and provided high precision in standard error estimation.From the findings, electrochemical measurements have shown that the presence of acetic acid affects predominantly the cathodic reaction and increased the rate of corrosion, which is agreed well with the general understanding of the CO_2 corrosion process.

ABSTRAK

Kehadiran asid asetik (HAc) dalam pembentukan air takungan minyak dan gas telah lama disyaki menyumbang kepada kadar hakisan CO_2. Model ramalan telah dibangunkan berdasarkan teori mekanistik yang mana melibatkan asas tindak balas elektrokimia untuk proses separa katod dan anod pada permukaan logam. Dengan menggunakan model ramalan ini, kelakuan kakisan keluli karbon dengan kehadiran HAc dalam kombinasi dengan pH dan suhu pada masa yang sama telah disiasat. Model ramalan kakisan ini telah disahkan dengan membandingkan pengiraan kadar hakisan dengan data karat yang diperolehi daripada pelbagai sumber kesusasteraan dan perisian ramalan kakisan dan ia menunjukkan hubungan yang baik dalam hubungan regresi dan member ketepatan yang tinggi berdasarkan anggaran piawai ralat. Daripada hasil kajian, ukuran elektrokimia telah menunjukkan bahawa kehadiran asid asetik menjejaskan kebanyakannya tindak balas katod dan peningkatan kadar hakisan, yang mana telah bersetuju dengan pemahaman umum proses hakisan yang CO_2.

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LIST OF SYMBOLS

α_c	Symmetry Factor
η	Overpotential
ΔH	Enthalpy of Activation
b	Tafel Slope
E_{corr}	Corrosion Potential
E_{rev}	Reversible Potential
f	Flow Factor
F	Faraday Constant
i_a	Activation Current Density
i_{corr}	Corrosion Current Density
i_{lim}	Limiting Current Density
i_o	Exchange Current Density
i_o^{ref}	Reference Exchange Current
k_m	Mass Transfer Coefficient
k_r	Rate of Reaction Constant
r^2	Coefficient Determination
T_{ref}	Reference Temperature

LIST OF ABBREVIATIONS

aq	Aqueous Phase
CO_2	Carbon Dioxide
CR	Corrosion Rate
DW	De Waard
ECE	Electronic Corrosion Engineer
Fe	Iron
Fe_3C	Iron Carbide
$FeCO_3$	Iron Carbonate
FeS	Iron Sulfide
g	Gas Phase
H_2	Hydrogen
HAc	Acetic Acid
mmpy	Millimeters per Year
PPM	Part per Million
R	Universal Gas Constant
S	Supersaturation
T	Temperature

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

In the formation water of oil and gas reservoirs the presence of organic acid species has long been suspected to contribute to the CO_2 corrosion rate. The effect has been considered to be secondary until new discoveries about the 80's and 90's the presence of acetic acid species showed the increased corrosion rate in CO_2 environment.

Model CO_2 corrosion prediction has been developed in many ways. These CO_2 corrosion prediction models can be divided into three categories that are empirical, semi-empirical and mechanistic models (Lee, 2004). Some recent models have been based on the underlying empirical CO_2 corrosion process. It has been done several studies on the empirical that occurs on carbon steel related to CO_2 corrosion. In the process of corrosion involves electrochemical, chemical processes and the processes transfer times occur simultaneously.

Prediction of corrosion behavior is an important concern in oil and gas industries. In design stage, corrosion prediction is used to select materials for construction and to maintain operations integrity. The prediction is also used to find better condition and improve the utilities. There are many CO_2 corrosion prediction models developed by industries. Such prediction models, basically, give accurate predictions. However, it has to be emphasized that those prediction model is valid only in certain conditions. It is not surprised when the same data will give different

results. Thus, it is needed a further study of each model developed by industries to gain insight understanding of the model backgrounds (Yuli, 2010).

1.2 PROBLEM STATEMENT

The actual condition affecting CO_2 corrosion carries difficulty in the experiment and simulation to predict corrosion rate based on empirical method. By using empirical method, modeling interactions effects between the species and the operational conditions at the same time, require not only a large number of experiment but also lack in statistical analysis and graphical data that support the conclusion. Besides, there are limited corrosion prediction model in the literature to compute the mixed variables simultaneously and no expressions were previously developed to express the corrosion model in CO_2 environment.

Thus, mechanistic modeling and simulation should be prepared because extreme condition in actual situation make difficult to do experiments. For that reason, it is important to develop the CO_2 corrosion model that supported by either solid fundamental theory or supported analytical background which can express relationship among the operational conditions (temperature and pH) and reservoir species (HAc).

1.3 OBJECTIVES

The aim of this study is to enhance a better understanding of the influence of HAc on corrosion in CO_2 environment, and their roles in contributing to corrosion rate at the same time. The work that will be used to accomplish the following specific objectives:

(i) Study the effects of acetic acid in combination with pH and temperature at the simultaneously steel corrosion in CO_2 environment.

(ii) Modelling CO_2 corrosion within the presence of acetic acid based on mechanistic theories.

(iii) Make comparison between model prediction and corrosion prediction software's available in industries, and experimental data.

1.4 SCOPES

The study investigated corrosion rate in CO_2simulated environmental containing HAc in several pH and temperature. Discussion of various parameters in the model related to the corrosion mechanism was based on the industrial corrosion software and available published experimental data.The scopes can be summarized as:

(i) The range of HAc concentration used in this study is 0-200 ppm.

(ii) The temperature and pH range tested in this study is 25 ^{0}C – 85 ^{0}C and pH 4 – pH 6.

(iii) The corrosion model had been developed is based on mechanistic theories.

(iv) The corrosion prediction has been verified with previous experimental data and corrosion prediction software's which are Freecorp, Cassandra, NORSOK and ECE.

CHAPTER 2

LITERATURE REVIEW

2.1 CO_2 CORROSION

In the oil and gas industry, carbon dioxide corrosion of carbon steel is a major problem. The presence of dry CO_2 gas or only oil is itself not corrosive. However, corrosion and subsequent failures cause by the contact of the surface of the metal with the aqueous phase. The work done in the past few decades have made the basic CO_2 corrosion reactions well understood and accepted (Nesic et al. 1995). The main chemical reactions include CO_2 dissolution and hydration to form carbonic acid,

$$CO_2\ g \Leftrightarrow CO_2\ (aq) \quad (2.1)$$

$$CO_2\ (aq) + H_2O \Leftrightarrow H\ CO_3 \quad (2.2)$$

Carbonic acid dissociates to form bicarbonate which also dissociates to give carbonate and hydrogen ions.

$$H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \quad (2.3)$$

$$HCO_3^- \Leftrightarrow H^+ + CO_3^{2-} \quad (2.4)$$

The overall electrochemical reaction of CO_2 corrosion is given by:

$$Fe + CO_2 + H_2O \Leftrightarrow FeCO_3 + H_2 \quad (2.5)$$

Thus, CO_2 corrosion can form the formation of a corrosion product, $FeCO_3$ which when initiated can form a protective or a non-protective scale depending on

conditions of the environment. The electrochemical reactions at the steel surface include the anodic dissolution of iron:

$$Fe \rightarrow Fe^{2+} + 2e^{-} \quad (2.6)$$

and two chatodic reactions. The chatodic reactions are proton reduction reaction and the direct reduction of carbonic acid:

$$2H^{+} + 2e^{-} \rightarrow H_2 \quad (2.7)$$

$$2H_2CO_3 + 2e^{-} \rightarrow H_2 + 2HCO_3^{-} \quad (2.8)$$

Although more than three decades of tough research, it is still unknown which of the two reactions actually exist on the surface. Therefore, many have taken that the total currents of the two reactions is from the net cathodic current. It has been suggested that at higher pH the direct reduction of bicarbonate ion becomes important. Having outlined the mechanism, one can anticipate that there are many environmental factors such as solution chemistry, pressure, pH, flow velocity, temperature etc., and affect the uniform CO_2 corrosion rate of mild steel. The formation of the corrosion product scales due to the environmental conditions could also have a significant effect on the corrosion rate of the metal. Some of the important factors that the effect CO_2 corrosion in the oil and gas industry will be discussed the next subchapters.

2.2 FACTORS AFFECTING CO_2 CORROSION

2.2.1 The Effect of pH

In corrosion process, pH is one of the important parameters. Usually, corrosion rate will be lower at higher pH. The pH of a wet gas in CO_2 system is often assumed as equal to the saturation of $FeCO_3$ precipitation. The pH can also be calculated by involving the concentration of species such as CO_2, H_2CO_3, HCO_3^{-}, CO_3^{2-}, H_2S, HS^{-}, S^{2-}, H^{+}, OH^{-}, H_2O, Fe^{2+} , CH_3COOH (acetic acid), CH_3COO^{-}. Sometimes, pH calculation can be done by incorporating the $FeCO_3$ precipitation

kinetics. The pH is also influenced by H^+ ions concentration, temperature, pressure, and ionic strength, thus pH in real conditions can be different from the calculated pH. Dissolved iron bicarbonate as the initial corrosion product will also contribute to increase the pH of solution.

An increase in pH will cause the film to become thicker, more dense and protective. Passivity of carbon steel is in the pH range of the carbonate/bicarbonate formation. Hoffmeister and Scheidacker (2004) recorded that at pH 5.8 the corrosion rate did not reduce significantly, which reflected a relatively porous, detached and unprotective scale. This may be related to fast formation of the scale.

pH of the fluid is calculated as initial pH of water and CO_2 only, which is expressed in the following:

$$pH_{CO_2} = 3.71 + 0.00417T - 0.5LOG(pCO_2) \quad (2.9)$$

The saturation pH is calculated as the smallest value according to the equation below:

$$pH_{ads} = 1.36+1307/T+273-0.17Log(fCO_2) \quad (2.10)$$

2.2.2 The Effect of Temperature

Temperature will affects the conditions for formation of the protective carbonate layers and affects corrosion rate in a different manner. The solubility of $FeCO_3$ is high and the precipitation rate is slow at temperatures below than 60 °C, so that protective films will not form until the pH is increased more than solubility product (Hoffmeister and Scheidacker, 2004). Above 60 °C the solubility of $FeCO_3$ decreases and the protectiveness of the iron carbonate layer increases with temperature; thus, the corrosion rate is reduced.

Temperature affects corrosion rate in a different manner, at temperatures below 60 ^oC, hydrogen evolution acts as the rate determinating step. At temperatures

above 100 °C, there is a direct reaction between steel and water (Schikorr reaction) to produce dense and protective films (Schmitt and Horstemeier, 2006) but carbon steel will face problems with pitting and stress corrosion cracking (Halvorsen and Sontvedt, 2006) because, carbonate film is formed rapidly at 80 °C.

The protective film will form at the temperatures greater than 60 °C, called the scaling temperature. The temperature where corrosion rate reaches a maximum value is called scaling temperature. At this temperature, Fe concentration forms at the metal surface to produce protective film. The scaling temperature is affected by gas flow rate and pH, where higher flow rate and lower pH will produce higher scaling temperature. The correlation between scaling temperature and partial pressure of CO_2 is expressed as in Equation 2.24 below (Halvorsen and Sontvedt, 2006):

$$T_{scale}= 2400/(6.7+0.6Log(fCO_2)) \quad (2.11)$$

Where T_{scale} is scaling temperature, fCO_2 is a correction factor for T defined as:

$$F_{scale}= (2400/T)-0.6Log(fCO_2)-6.7 \quad (2.12)$$

What is Fscale.

- F_{scale} is set to 1 if formation water is present or when a superficial gas velocity is above 20 m/s.

2.3 EFFECT OF ACETIC ACID

Since the 1980's, the influence of HAc on the corrosion rate of carbon steel in oilfield brines containing CO_2 is well documented in literature and has been the subject of many studies. As early as 1983, presence of acetic acid in the brine will increase the corrosion rate of carbon steel significantly have been reported by Crolet and Bonis (1983). The effect of HAc on CO_2 corrosion is to either increase or decrease corrosion strongly depending on pH and temperature. However, research on the effect of HAc in CO_2 system is still limited. In the literature, the effects of those factors are debatable and sometime contradictory. For that reason, it is important to

improve the understanding the effect ofCO_2 and Acetic Acid on carbon steel corrosion (Yuli, 2010).

2.3.1 Chemistry of Acetic Acid

CH_3COOH is the structural formula for Acetic Acid (HAc). It is a weak acid that does not completely dissociate in aqueous solutions. It has been reported that free acetic acid could increase the corrosion rate (Martin, 2009). The mechanism of dissolved acetic acid in CO_2 corrosion can be correlated to the undissociated HAc concentration present in the brine (George and Nesic, 2004). Laboratory tests have validated that dissociated acid can alter the corrosion rate in CO_2 environment conducted by Garsany et al. (2004). The dissociation of HAc in water occurs according to the equations below (Nafday, 2004):

$$HAc_{(aq)} + H_2O \Leftrightarrow H_3O^+_{(aq)} + A^-_{(aq)} \quad (2.13)$$

Then the aqueous HAc partly dissociation into hydrogen and acetate ions:

$$HAc\ (aq) \Leftrightarrow H^+\ (aq) + Ac^-\ (aq) \quad (2.14)$$

$$H^+\ (aq) + e^- \rightarrow \tfrac{1}{2}\ H_2(g) \quad (2.15)$$

The equilibrium constant for HAc dissociation, K_{HAc} is:

$$K_{HAc} = \frac{[H^+][Ac^-]}{[HAc]} \quad (2.16)$$

The overall corrosion reaction for carbon steel with the presence of acetic acid in the CO_2 environment is:

$$Fe + H_2CO_3 \rightarrow FeCO_3 + H_2 \quad (2.17)$$

$$Fe + 2HAc \rightarrow Fe(Ac)_2 + H_2 \quad (2.18)$$

The dependency of acetic acid equilibrium constant on temperature is expressed in the following formula (Nafday, 2004):

$$K_{HAc} = 10^{-(6.66104-0.0134916*Tk+2.37856*10-5*Tk2)} \quad (2.19)$$

The rate of reaction involving CO_2 and acetic acid is believed to be limited by the preceding slow hydration of CO_2 (Nafday, 2004):

$$CO_2 + H_2O \rightarrow H_2CO_3 \text{ (aq)} \quad (2.20)$$

The reaction mechanism and kinetics of the overall reactions are influenced by acetic acid concentration, CO_2 partial pressure, pH, and water contaminants.

2.3.2 Corrosion Mechanism of Acetic Acid

The effect of acetic acid on the corrosion of mild steel has been studied by several of researchers. Crolet et al. (1999) stated that CO_2 result of acidification also can cause the partial re-association of anions. Such weak acids will raise the limiting diffusion current for cathodic reduction then increase the oxidizing of H^+. The presence of this acid also will tend to solubilise the dissolving iron ions.

The electrochemical behavior of carbon steel on the additions of HAc has shown that the presence of HAc in the solution decreases pH, increases the cathodic limiting current, and decreases E_{corr}. In this condition, the cathodic reaction will become the rate determining step. The limitation is due to diffusion of proton to the steel surface rather than electron transfer. In general, it has been agreed that HAc can increase the cathodic reaction rate (hydrogen evolution reaction) if the concentration is significant.

The study of the effect of acetate ions on the rates and mechanisms of corrosion by using a rotating disc electrode (RDE) on surfaces free film using voltametry, have been published by Garsany et al. (2002). They found a figure that can be attributed to reduction of HAc and hydrogen ion on steel surface. They argued

that as HAc dissociation can happen very quickly, it is not possible to differentiate the direct HAc reduction from reduction of hydrogen ions at the electrode surface. They argued that the increase rate of corrosion for HAc in CO_2 environment must be proportional to the undissociated acetic acid concentration in the brine. They emphasized that the electrochemistry of acetic acid at steel cannot be distinguishable from free proton because of its rapid dissociation. This conclusion was recorded after they used a rotating disk electrode to study the effect of Acetate ions on the rate of corrosion usingcyclic voltammetry.

The work of Crolet et al. (1999) suggested that the presence of HAc will inhibited the anodic (iron dissolution) reaction. Have conducted an experiment on low HAc concentrations (6 - 60 ppm). They found that the presence of HAc increased rate of corrosion due to an inversion in the bicarbonate/acetate ratio. At this inversion point, HAc is the main source of acidity since it is the predominant acid compared to carbonic acid.

2.3.3 Effects of Acetic Acid on Carbonate Film Formation

An investigation the role of HAc in corrosion rate on film formation was done by Crolet et al. (1999). The experiment succeeded in creating a film on the steel surface after exposing the specimen for three days at a temperature of 80 ^{0}C and high pH. He used LPR and EIS corrosion measurement methods to identify the effect of anodic reactions and HAc on the cathodic of CO_2 corrosion. He concluded that HAc affects the limiting current and do not affect the charge transfer mechanism of cathodic reaction. HAc acts as a source of hydrogen ions and HAc needs an activation time for its actionat room temperature (22 ^{o}C).

The role of acetic acid/ion can retard the time to reach scaling temperature have been observed by Vennesa et al. (2007). They related this effect as an increase in the corrosion area. This argument was supported by experimental observations which showed a reduction in corrosion rate in experiments without Acetate ion. There was proof that Acetate ion can attack existing iron carbonate films and make them thinner. The pitting corrosion will happen if the attack was localized, because

of local film would be thinning. The results on the role of acetate in CO2 corrosion was by published Hedges and McVeigh (1999). Experiments was performed using rotating cylinder electrodes, both sodium acetate and HAc as a source of acetate ions in various media (two synthetic oilfield brines and 3% NaCl). Both sources of acetate ions shown to increase the corrosion rate, while sodium acetate increased the pH and acetic acid decreased it. The formation of thinner iron carbonate films will cause the increased corrosion rates since acetate ions have the ability to form iron acetate and remove iron away from the steel surface.

2.4 CORROSION PRODUCT FILM FORMATION

During the corrosion process, the types of corrosion product film formed on the surface of the metal will strongly effect the CO_2 corrosion of a metal. The protectiveness, stability, precipitation rate and the adherence of these films decide the result of (localized/ uniform) and the corrosion rate. Corrosion films can be divided into main elements that are Iron carbide (Fe_3C), Iron carbonate ($FeCO_3$) and Iron sulfide (FeS).

2.4.1 Iron Carbide (Fe_3C)

Iron carbide do not dissolved component of the mild steel, which is left behind from the corrosion process. It is conductive, very porous and non-protective. Iron carbide films can significantly affect the corrosion process by either decreasing the corrosion rate by acting as a diffusion barrier or increasing the corrosion due to galvanic coupling of the film to the metal, increase in the true specimen surface area and acidification of the solution inside the corrosion product film (Lee, 2004).

2.4.2 Iron Carbonate ($FeCO_3$)

The reaction for formation of solid iron carbonate is given by (Lee, 2004) :

$$Fe^{2+} + CO_3^{2-} \Leftrightarrow FeCO_3(s) \qquad (2.21)$$

The precipitation of solid iron carbonate occurs when the product of concentrations of Fe^{2+} and CO_3^{2-} exceed a certain limit known as the solubility limit. However, the rate of precipitation of iron carbonate is so slow that most often the precipitation kinetics comes into consideration rather than the thermodynamics. The equation for the rate of precipitation of the iron carbonate ($R_{FeCO3(S)}$) is given as:

$$R_{FeCO3(S)} = \frac{A}{V} f(T).\, Ksp_{FeCO_3}.\, f(S_{FeCO_3}) \tag{2.22}$$

Where Supersaturation S is defined as:

$$S_{FeCO_3} = \frac{c_{Fe^{2+}} c_{CO_3^{2-}}}{Ksp_{FeCO_3}} \tag{2.23}$$

With A/V = the surface area-to-volume ratio and Ksp_{FeCO_3} = solubility limit of $FeCO_3$ Since CO_3^{2-} ion concentration is dependent on the pH, it can be assumed that:

$$S = f\,(Fe^{2+}, pH) \tag{2.24}$$

When steel surface precipitates by the iron carbonate, the corrosion rate decrease by presenting a diffusion wall for the species involved in the corrosion process and also blocking the steel portion and preventing electrochemical reactions from occurring.

The temperature and supersaturation is most important factors in disturbing the precipitation of iron carbonate.

2.4.3 Iron Sulfide (FeS)

The formation of iron sulfide only occurs in the presence of H_2S. The reaction for formation of solid iron carbonate is given by (Lee, 2004):

$$Fe^{2+} + S^{2-} \Leftrightarrow FeS(s) \tag{2.25}$$

It has been assumed that the precipitation of solid iron sulfide occurs when the product of Fe^{2+} and S^{2-} concentrations go beyond the solubility limit of FeS. The equation for the rate of precipitation of the iron carbonate ($R_{FeS(S)}$) is given as:

$$R_{FeCO3(S)} = \frac{A}{V} f(T).\, Ksp_{FeS}.\, f(S) \tag{2.26}$$

Where Supersaturation S_{FeS} is defined as:

$$S_{FeS} = \frac{c_{Fe^{2+}} c_{S^{2-}}}{Ksp_{FeS}} \tag{2.27}$$

With Ksp_{FeS} = solubility limit of FeS

It is assumed that iron sulfide affects the CO_2 corrosion in the same way as iron carbonate (by being a diffusion barrier and surface blockage). However, iron sulfide films are semi-conductive; in some cases it has been observed that the presence of iron sulfide may lead to localized corrosion and the cause is still not clear (Lee, 2004).

2.5 CORROSION PREDICTION MODELS

Models to calculate corrosion rate in CO_2 gas environments have many different approach. Each model predicts corrosion rate in different manner. They used parameters and formula based on literatures and their own experience. There are many equations that give certain predictions of corrosion rates for CO_2 environments. These include the de Waard and Milliam (1975) and it's many subsequent derivatives, Sun and Hong, (2002), Vera and Hernandez (2006) and Nesic et al. (2002). All of these were developed from different systems and assumptions.

During the last decade, the models were developed by involving limited variables. Recently, new variables are indicated having contributions in corrosion models. For examples, it has been demonstrated that flow can enhance the corrosion

process. Based on that theory, the models tried to cover these factors de Waard et al (1995). The other factors, still in investigations, are effects of scaling product, effects of oil properties, inhibitors, and other species contaminants (H_2S, HAc, and naphthanic acid). The work done by de Waard and Milliam (1975) was carried out in stirred beakers at atmospheric conditions with carbon dioxide gas being bubbled through water. The equation they developed showed solely the effects of chemistry on the maximum corrosion rate and these give a reasonable estimate of the corrosion rate in a stagnant system with no corrosion product being present.

In subsequent considerations, many factors were added and de Waard et al. (2001) provided correction factors that which to account for the gas fugacity, the protective iron carbonate films formation, the effect of ferrous ions on the pH, the presence of oil, and the effect of condensing water.

2.6 COMMERCIAL CORROSION PREDICTION MODEL

2.6.1 ECE (Electronic Chemical Engineering)

ECE program software calculates corrosion rate based on the modified de Waard and Milliam (1975) method. **ECE** model includes oil wetting correlation based on field correlation. For low horizontal flow velocities < 1 m/s, the F_{oil} =1. ECE proposes a corrosion prediction expression as follows:

$$V_{cor} = \frac{1}{\frac{1}{V_r} + \frac{1}{V_m}} \tag{2.28}$$

Where, V_r is corrosion reaction and V_m is mass transfer effect. The corrosion reaction can be calculated using the following equation:

$$\log V_r = 4.84 - \frac{119}{t + 273} + 0.581\log(fCO_2) - 0.34(pH_{act} - pH_{CO_2}) \tag{2.29}$$